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Thermoosmosis and Transported Entropy of Water across Hydrocarbonsulfonic Acid-Type Cation-Exchange Membranes

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Solvent transport across hydrocarbonsulfonic acid-type cation-exchange membranes was measured for aqueous electrolyte solutions under a temperature difference and an osmotic pressure difference. The hydrocarbonsulfonic acid-type cation-exchange membranes, Aciplex® K-181, Aciplex® K-182, and Neosepta® C66-5T with the H^+, Li^+, Na^+, K^+, NH_4^+, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$, $(CH_3)_3NH^+$, $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, $(n\text{-}C_3H_7)_4N^+$, and $(n\text{-}C_4H_9)_4N^+$ forms were used. The direction of thermoosmosis across the membranes with the H^+ and the Na^+ forms was from the cold side to the hot side, as observed for various anion-exchange membranes. However, the direction was from the hot side to the cold side for the membranes with the ammonium and the alkylated ammonium ion forms, except for Neosepta® C66-5T with the $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, and $(n\text{-}C_3H_7)_4N^+$ forms. This is why the entropy of the water in the membranes will increase with increasing the number of hydrogens combining with the nitrogen of the alkylated ammonium counterions, because they are exchangeable with the hydrogens of water molecules in the membranes. Thermoosmosis across the membranes with the $(n\text{-}C_3H_7)_4N^+$ and the $(n\text{-}C_4H_9)_4N^+$ forms will also occur toward the cold side, because the hydrophobic interaction between the hydrophobic alkyl groups of the counterions and the membrane matrix is very strong and the membranes act as a hydrophobic polyethylene membrane.

Thermoosmosis occurs from the cold side to the hot side for anion-exchange membranes with various counterions,[1,2] whereas for cation-exchange membranes the direction of thermoosmosis varies with the counterions.[3—5] In a previous paper,[6] we studied the dependence of the thermoosmotic coefficient on the species of counterions for the perfluorosulfonic acid-type membrane, Flemion® S. Thermoosmosis across Flemion® S with the ammonium and the alkylated ammonium ion forms was dependent systematically on the number of hydrogens combining with the nitrogen of the counterions and on the bulk of the alkyl groups of counterions. In this paper, therefore, we report the dependence of the thermoosmotic coefficient on the species of counterions for hydrocarbonsulfonic acid-type cation-exchange membranes.

If cation-exchange membranes have ideal permselectivity for counterions, the volume flux, J_v, across the membranes due to a temperature difference, ΔT, and an osmotic pressure difference, $\Delta\pi$, can be written as[7]

$$-J_v = D^*\{(\bar{\bar{s}}_0 - s_0)\Delta T - v_0\Delta\pi\}, \tag{1}$$

where

$$\begin{aligned} D^* &= (1/\delta)(\bar{c}_0 f \ell^\circ_{v0} - \tau_0 F\phi X f \ell^\circ_{v+}) \\ &= fD^{*\circ}. \end{aligned} \tag{2}$$

The subscript 0 refers to water molecules, $\bar{c}_0$ is the concentration of water in the membrane phase, τ_0 the reduced transport number of water, s_0 the partial molar entropy of water in the external solution, $\bar{\bar{s}}_0$ the mean molar transported entropy of water in the membrane, v_0 the partial molar volume of water, δ the thickness of the membrane, F the Faraday constant, and ϕX is the effective concentration of fixed charges. The ℓ°_{v0} and the ℓ°_{v+} are parameters related to the mobility of water in the membrane and related to the interaction between the cations and water, and f is the tortuosity factor depending on the tortuosity and porosity of the membrane.[8,9] In general, we assume that

$$f \propto (\phi^\circ)^{2/3}/(\phi^\circ)^{1/3} = (\phi^\circ)^{1/3}, \tag{3}$$

where ϕ° is the volume fraction of the liquid phase in the membrane.

If there is no osmotic pressure difference, Eq. 1 becomes

$$-J_v = D\Delta T, \tag{4}$$

where

$$D = fD^\circ = (\bar{\bar{s}}_0 - s_0) f D^{*\circ}. \tag{5}$$

Moreover, if there is no temperature difference, Eq. 1 becomes

$$-J_v = L_p \Delta\pi, \tag{6}$$

where

$$L_p = -v_0 D^* = -v_0 f D^{*\circ}. \tag{7}$$

Therefore, if we experimentally obtain the values of D and D^*, we can estimate the value of the entropy difference $(\bar{\bar{s}}_0 - s_0)$:

$$\begin{aligned}\bar{\bar{s}}_0 - s_0 &= -v_0 D/L_p \\ &= D/D^*.\end{aligned} \tag{8}$$

The value of the difference in the molar enthalpy of water between the membrane and the external solution at steady state can be written as $\Delta h_0 = -T(\bar{\bar{s}}_0 - s_0)$.

Experimental

Membranes. The hydrocarbonsulfonic acid-type cation-exchange membranes, Aciplex® K-181 and K-182 (Asahi Chemical Industry Co., Ltd.), and Neosepta® C66-5T (Tokuyama Soda Co., Ltd.), were used. The membrane, Aciplex® K-182, was made by treating the surfaces of Aciplex® K-181 with polyelectrolytes in order to improve the permselectivity for monovalent and divalent cations. The Neosepta® C66-5T was prepared by the paste method.[10] The paste consisted of styrene, DVB, benzylperoxide, and fine PVC powder, and the treatment to introduce ion-exchange groups was sulfonation with concentrated sulfonic acid. Ion-exchange capacities were measured by titrating the amount of H^+ ions released from the H^+ form membrane immersed in 1 mol kg^{-1} NaCl solution. The ion-exchange capacity and the water content of membranes are expressed by the unit: mmol of ion-exchange groups per g of the dry membrane without the weight of the anhydrous counterions and g of water per g of the dry membrane without the weight of the anhydrous counterions, because of the weight of dry membrane including the weight of counterions varies with the species of the counterions. The membrane thickness, ion-exchange capacity, and the transport numbers of counterions calculated from the concentration membrane potential of 0.1//0.2 mol kg^{-1} are listed in Table 1.

Electrolyte Solutions. The reagents used for the preparation of aqueous HCl, LiCl, NaCl, KCl, NH_4Cl, CH_3NH_3Cl, $(CH_3)_2NH_2Cl$, $(CH_3)_4NCl$, $(C_2H_5)_4NBr$, $(n\text{-}C_3H_7)_4NBr$, and $(n\text{-}C_4H_9)_4NBr$ solutions were special grades and for that of $(CH_3)_3NHCl$ was first grade from Wako Pure Chemical Industries, Ltd., Japan.

Measurements of Thermoosmosis. The volume flux under a temperature difference was measured using the same thermoosmosis cell as that used in the previous paper.[6] The upper section, which is a hot chamber (1500 cm^3), was larger than the lower, a cold chamber (96 cm^3). The effective area of the membrane was 28 cm^2. The two temperatures in the cold side and the hot side were controlled to fix the mean temperature at 308.2 K. The relationship between the effective temperature difference across the membrane, ΔT, and the temperature difference of two bulk solutions, ΔT_b, has already been reported and $\Delta T/\Delta T_b$ was 0.70 to 0.73 for various usual membranes.[1] Therefore, we also assume that $\Delta T = 0.7\Delta T_b$ in this work. All measurements were carried out at 0.01 mol kg^{-1} of electrolyte solutions.

Measurements of Osmotic Volume Flux. The volume flux under an osmotic pressure difference was measured using the same cell as that used in the previous paper.[6] The effective area of the membrane was 2.54 cm^2. The cell was placed in an air thermostat and the temperature was kept at 298.16±0.5 K. The concentration of the external salt solution on one side of the membrane was fixed at 0.001 mol dm^{-3}, and that on the other side was varied in the range of 0.05 to 0.5 mol dm^{-3}.

Measurements of Membrane Resistance. Membranes were equilibrated at 0.01 mol kg^{-1} of the ammonium and the alkylated ammonium halide solutions. Two flat, impervious carbon electrodes were directly connected to both sides of the membrane equilibrated with the solution and the membrane resistance was measured at 25 °C with 10 kHz using an LF Impedance Analyzer 4192A (Yokogawa-Hewlett-Packard, Ltd., Japan). The effective area of membrane was 1 cm^2.

Results and Discussion

Figure 1 shows examples of the movement of the liquid meniscus, d, against time, t, for Aciplex® K-181 with the H^+ form in 0.01 mol kg^{-1} of HCl solution, where the mean temperature was kept at 308.2 K and the temperature differences of the bulk solutions, ΔT_b, were 3 to 9 K. Thermoosmosis was calculated from the slopes of these figures.

Figure 2 shows linear relationships between the volume flux, J_v, and the temperature differences of the bulk solutions, ΔT_b, for Aciplex® K-181 and K-182 with the H^+, Li^+, Na^+, and K^+ forms. For Neosepta® C66-5T with these ion forms, thermoosmotic data was

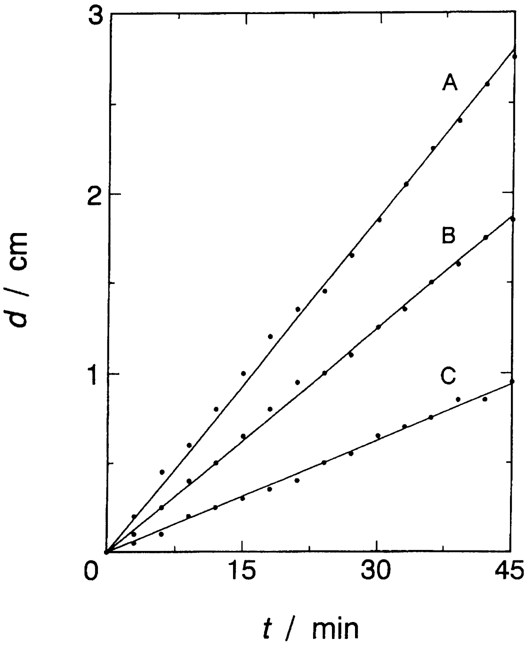

Fig. 1. Examples of the movement of liquid meniscus, d, against time, t, under temperature differences for Aciplex® K-181 with the H^+ form in 0.01 mol kg^{-1} of HCl solution. Temperature differences (K): A, 9; B, 6; C, 3.

Table 1. The Properties of Various Membranes

Membranes	Membrane thickness	Ion-exchange capacity[a)]	Molality of fixed charge[a)]	Transport number[b)]
	10^{-1} cm	mmol/g dry-membr.	mmol/g H_2O	
Aciplex® K-181	0.094	1.38	4.93	0.99
Aciplex® K-182	0.093	1.26	4.84	0.99
Neosepta® C66-5T	0.140	2.15	4.78	1.00

a) K^+ form. b) Calculated from the membrane potential in 0.1//0.2 mol kg^{-1} KCl solutions.

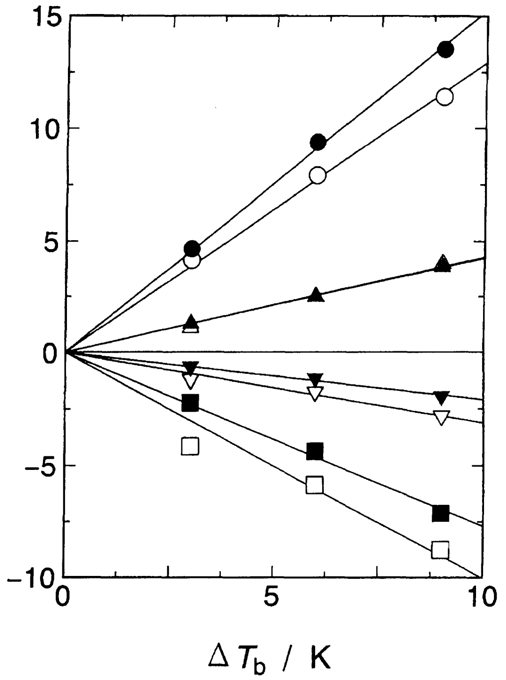

Fig. 2. The dependence of thermoosmotic volume flux, J_v, on the temperature difference of bulk solutions, ΔT_b, for Aciplex® K-181 with the H^+ (○), Li^+ (□), Na^+ (△), and K^+ (▽) forms and Aciplex® K-182 with the H^+ (●), Li^+ (■), Na^+ (▲), and K^+ (▼) forms at the mean temperature 308.2 K.

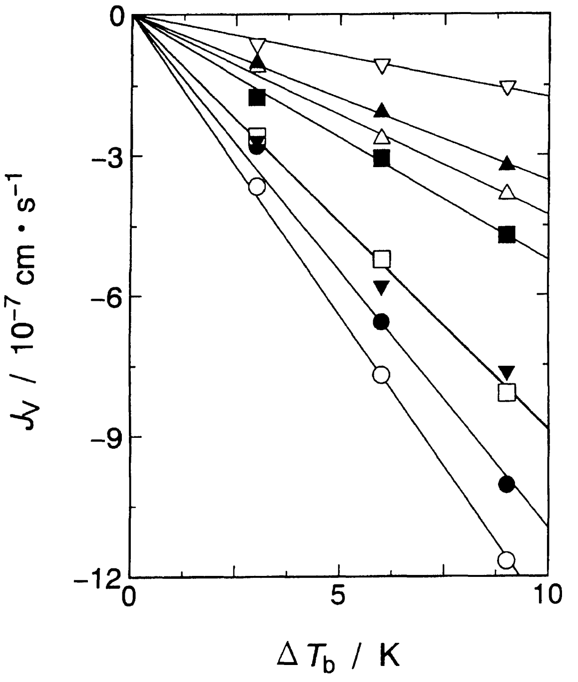

Fig. 3. The dependence of thermoosmotic volume flux, J_v, on the temperature difference of bulk solutions, ΔT_b, for Aciplex® K-181 with the ammonium and the alkylated ammonium ion forms at the mean temperature 308.2 K. Electrolytes: ○: NH_4Cl, ●: CH_3NH_3Cl, □: $(CH_3)_2NH_2Cl$, ■: $(CH_3)_3NHCl$, △: $(CH_3)_4NCl$, ▲: $(C_2H_5)_4NBr$, ▽: $(n\text{-}C_3H_7)_4NBr$, ▼ $(n\text{-}C_4H_9)_4NBr$.

already reported in Ref. 3. The positive sign of J_v means the directions of thermoosmosis toward the hot solution side. The direction of thermoosmosis for the H^+ and Na^+ forms was from the cold side to the hot side, whereas for the Li^+ and K^+ forms it was from the hot side to the cold side. The volume flux for the H^+ form was larger than that for the other ion forms, because the hydrogen ions can exchange with the hydrogen of the adjacent water molecules. The exchange contributes to the water transport across the membrane as the proton jumps in conductivity.[3,4,6)]

The state of water in the ion-exchange membranes is affected by the membrane matrix, fixed charges, and counterions. For anion-exchange membranes, both the membrane matrix and the fixed charges of quaternary ammonium ion act to order the structure of water and the entropy of water in the membranes will be lower than that in the external solutions. For cation-exchange membranes, the fixed charges of sulfonic acid groups act locally to disorder the structure of water, even though the charged polymer membrane act, as a whole, to order the structure of water.[11,12)] Therefore, the state of water in the cation-exchange membranes will be more influenced by the nature of the counterions than is the case for anion-exchange membranes. For Li^+ ions in free solutions, it is known that there are three states of water surrounding Li^+ ions: (1) heavily hydrated water, (2) disordered water layer, and (3) water similar to free water.[13)] For the membranes with the Li^+ form, the region of disordered water will be enhanced, and the direction of thermoosmosis will occur toward the cold side due to the increase of the entropy of water in the membranes.[4)] Similarly, for the membranes with the K^+ form, the region of disordered water will also be enhanced.

Figures 3, 4, and 5 show the linear relationships between the volume flux and the temperature differences of the bulk solutions for Aciplex® K-181, Aciplex® K-182, and Neosepta® C66-5T with the ammonium and the alkylated ammonium ion forms, respectively. The direction of thermoosmosis was all from the hot side to the cold side, except for Neosepta® C66-5T with the $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, and $(n\text{-}C_3H_7)_4N^+$ forms. The entropy of water in the membranes will increase with increasing the number of hydrogens combining with the nitrogen of the counterions because they are exchangeable with the hydrogens of water molecules in the membranes. Thermoosmosis for the NH_4^+ form was the lowest value, which means the greatest absolute value toward the cold side; it increases with decreasing the number of hydrogens combining with the nitrogen of the counterions. The highest value of thermoosmosis was observed for Aciplex® K-182 and Neosepta® C66-5T with the $(C_2H_5)_4N^+$ form and for Aciplex® K-181 with the $(n\text{-}C_3H_7)_4N^+$ form. Thermoosmosis was again decreased with increasing hydrophobicity of the counterions.

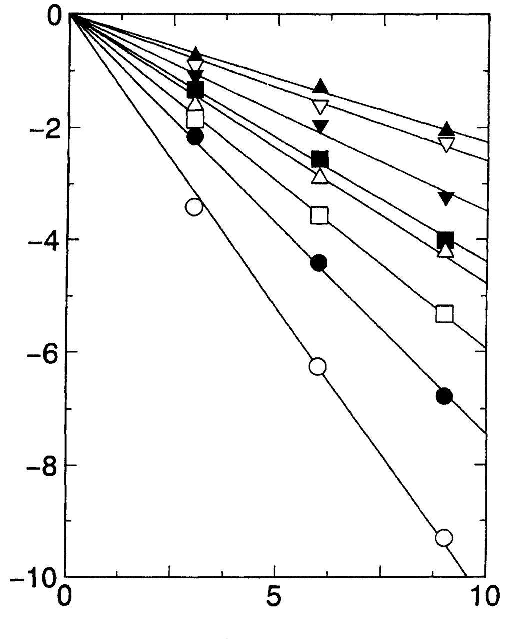

Fig. 4. The dependence of thermoosmotic volume flux, J_v, on the temperature difference of bulk solutions, ΔT_b, for Aciplex® K-182 with the ammonium and the alkylated ammonium ion forms at the mean temperature 308.2 K. Electrolytes: ○: NH_4Cl, ●: CH_3NH_3Cl, □: $(CH_3)_2NH_2Cl$, ■: $(CH_3)_3NHCl$, △: $(CH_3)_4NCl$, ▲: $(C_2H_5)_4NBr$, ▽: $(n\text{-}C_3H_7)_4NBr$, ▼: $(n\text{-}C_4H_9)_4NBr$.

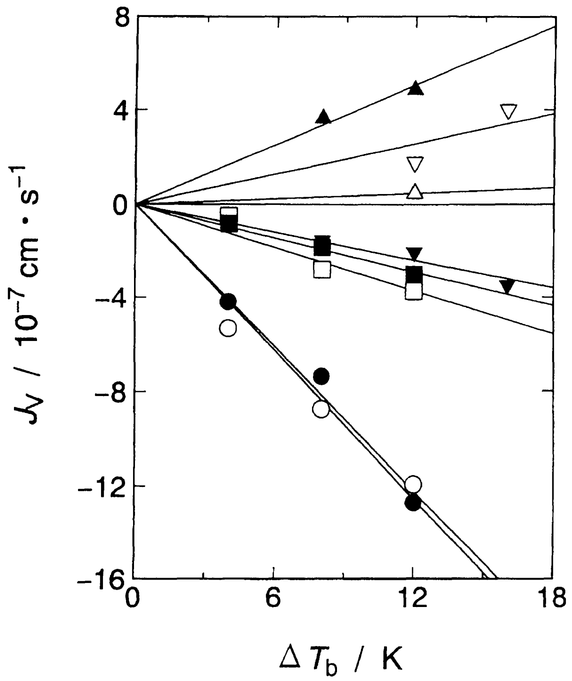

Fig. 5. The dependence of thermoosmotic volume flux, J_v, on the temperature difference of bulk solutions, ΔT_b, for Neosepta® C66-5T with the ammonium and the alkylated ammonium ion forms at the mean temperature 308.2 K. Electrolytes: ○: NH_4Cl, ●: CH_3NH_3Cl, □: $(CH_3)_2NH_2Cl$, ■: $(CH_3)_3NHCl$, △: $(CH_3)_4NCl$, ▲: $(C_2H_5)_4NBr$, ▽: $(n\text{-}C_3H_7)_4NBr$, ▼: $(n\text{-}C_4H_9)_4NBr$.

Figure 6 shows the membrane resistance, R_m, in the ammonium and the alkylated ammonium halide solutions against the friction coefficient of counterions, f_+, which is the reciprocal of the mobility. If the ions are spherical, the friction coefficients are proportional to the radii of ions. The membrane resistance slightly increased with increasing the hydrophobic alkyl groups of the counterions and for the $(n\text{-}C_3H_7)_4N^+$ and $(n\text{-}C_4H_9)_4N^+$ forms the membrane resistance became very high. The ratios of the membrane resistance with the alkylated ammonium ions to that with the ammonium ion were 1.53 to 814.82 for K-181, 1.43 to 465.37 for K-182, and 1.41 to 110.29 for C66-5T at the molality of 0.01 mol kg^{-1}, although the ratios of the friction coefficients of the alkylated ammonium ions to that of the ammonium ions in the free solutions are only 1.27 to 3.83. This suggests that the radius of counterions becomes large and the van der Waals attractive forces between the hydrophobic alkyl chain of counterions and membrane matrix become very strong. The membrane acts as a hydrophobic polyethylene membrane. Similar attractive

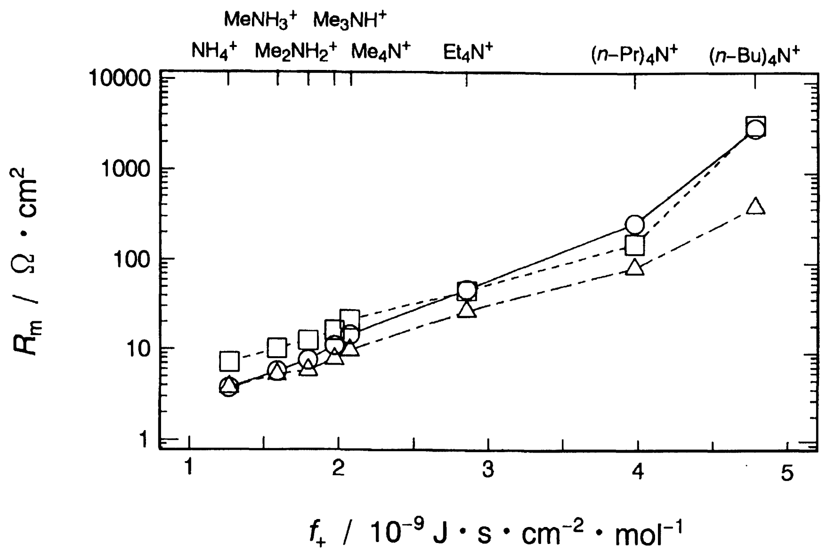

Fig. 6. The dependence of the membrane resistance, R_m, on the friction coefficient of counterions, f_+, for all membranes with the ammonium and the alkylated ammonium ion forms. Membranes: ○: Aciplex® K-181, □: Aciplex® K-182, △: Neosepta® C66-5T.

forces are known among long alkyl chains in polysoap.[14] Therefore, the entropy of water in the membranes will increase with increasing the hydrophobic alkyl groups of the counterions.

In order to estimate the difference between the mean molar transported entropy of water in the membrane phase, $\overline{\overline{s}}_0$, and the molar entropy of water in the external solutions, s_0, the volume flux was measured under an osmotic pressure difference. Figure 7 shows linear relationships between the volume flux and osmotic pressure difference for Aciplex® K-181 with the ammonium and the alkylated ammonium ion forms. Similar relationships were observed for Aciplex® K-182 and Neosepta® C66-5T with all the ion forms. The osmotic pressure difference of the external salt solutions was calculated from the concentration difference and osmotic coefficients in the literature[15,16] using Eq. 9:

$$\Delta\pi = \nu g R T \Delta c_s, \tag{9}$$

where ν is the number of moles of ions formed from 1 mole of electrolyte, g the osmotic coefficient, and Δc_s the concentration difference of the external salt solutions. The osmotic coefficients for CH_3NH_3Cl, $(CH_3)_2NH_2Cl$, and $(CH_3)_3NHCl$ were assumed to be 0.9 because of the lack of better data. The values of coefficient D^* were calculated from the slopes of these figures. The volume flux under an osmotic pressure difference decreases with increasing the alkyl groups of the counterions, because of decreasing the water content of membrane and/or increasing the bulky hydrophobic alkyl groups of counterions.

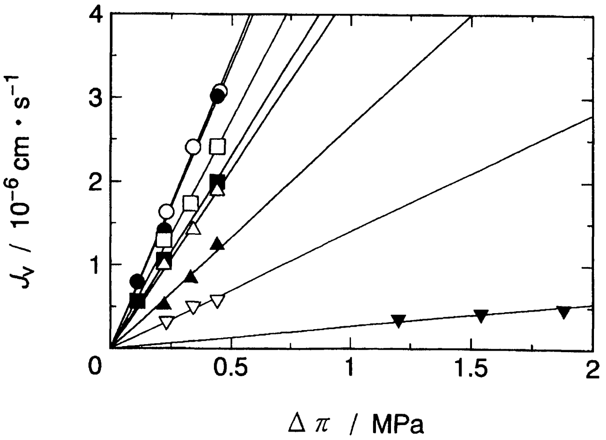

Fig. 7. The dependence of osmotic volume flow, J_v, on the osmotic pressure difference of the external salt solutions, $\Delta\pi$, for Aciplex® K-181 with the ammonium and the alkylated ammonium ion forms. Electrolytes: ○: NH_4Cl, ●: CH_3NH_3Cl, □: $(CH_3)_2NH_2Cl$, ■: $(CH_3)_3NHCl$, △: $(CH_3)_4NCl$, ▲: $(C_2H_5)_4NBr$, ▽: $(n\text{-}C_3H_7)_4NBr$, ▼: $(n\text{-}C_4H_9)_4NBr$.

The values of the entropy difference of water, $(\overline{\overline{s}}_0 - s_0)$, were estimated from Eq. 8 using the data of thermoosmotic coefficient, D, and the coefficient, D^*, these values are listed in Table 2. In order to study the dependence of D° on the counterions, $f_{Li}D^\circ$ which means the thermoosmotic coefficient at the same water content as that with the Li^+ form, was calculated. These values also listed in Table 2, where the volume fraction ϕ° was approximately evaluated by assuming $\phi^\circ = w_0/(1+w_0)$. The w_0 is the water content with the unit: g of H_2O per g of dry membrane without counterions. The order of D° is the same as that of D, because the variation in the water contents was comparatively small.

Figures 8, 9, and 10 show the dependence of thermoosmotic coefficients, $-D$, and the entropy difference of water, $-(\overline{\overline{s}}_0 - s_0)$, on the friction coefficient of the counterions, f_+, for Aciplex® K-181, Aciplex® K-182, and Neosepta® C66-5T, respectively. The alternation of

Table 2. The Values of w_0, $-D$, $-f_{\mathrm{Li}}D^{\circ}$, D^{*}, and $-(\bar{\bar{s}}_0-s_0)$ for Various Membranes

Membranes	Counterions	w_0	$-D$	$-f_{\mathrm{Li}}D^{\circ}$	D^{*}	$-(\bar{\bar{s}}_0-s_0)$
		g-H_2O/g-dry membr. without counterions	10^{-8} cm K^{-1} s^{-1}	10^{-8} cm K^{-1} s^{-1}	10^{-7} cm mol J^{-1} s^{-1}	J K^{-1} mol^{-1}
Aciplex® K-181	H^+	0.31	18.9	19.1	4.6	0.41
	Li^+	0.33	−14.8	−14.8	2.1	−0.71
	Na^+	0.30	5.8	6.0	2.5	0.23
	K^+	0.28	−4.8	−5.0	2.6	−0.19
	NH_4^+	0.26	−18.1	−19.2	3.9	−0.46
	$CH_3NH_3^+$	0.24	−15.0	−16.5	3.8	−0.39
	$(CH_3)_2NH_2^+$	0.24	−12.5	−13.8	3.1	−0.41
	$(CH_3)_3NH^+$	0.23	−7.7	−8.5	2.7	−0.29
	$(CH_3)_4N^+$	0.27	−5.9	−6.2	2.4	−0.24
	$(C_2H_5)_4N^+$	0.33	−5.0	−5.0	1.4	−0.35
	$(n\text{-}C_3H_7)_4N^+$	0.32	−2.6	−2.7	0.8	−0.33
	$(n\text{-}C_4H_9)_4N^+$	0.20	−12.9	−14.7	0.2	−8.26
Aciplex® K-182	H^+	0.27	22.0	22.5	3.3	0.66
	Li^+	0.29	−10.8	−10.8	1.8	−0.59
	Na^+	0.27	6.0	6.2	2.4	0.25
	K^+	0.26	−3.0	−3.0	2.6	−0.11
	NH_4^+	0.22	−15.3	−16.4	3.6	−0.42
	$CH_3NH_3^+$	0.20	−10.5	−11.5	3.3	−0.32
	$(CH_3)_2NH_2^+$	0.19	−8.6	−9.5	2.9	−0.30
	$(CH_3)_3NH^+$	0.21	−6.3	−6.8	2.6	−0.24
	$(CH_3)_4N^+$	0.23	−7.1	−7.4	2.2	−0.32
	$(C_2H_5)_4N^+$	0.27	−3.3	−3.4	1.0	−0.32
	$(n\text{-}C_3H_7)_4N^+$	0.27	−3.9	−4.0	0.7	−0.54
	$(n\text{-}C_4H_9)_4N^+$	0.20	−5.0	−5.4	0.9	−5.39
Neosepta® C66-5T	NH_4^+	0.41	−1.6	−1.7	4.7	−0.35
	$CH_3NH_3^+$	0.37	−1.4	−1.5	3.6	−0.41
	$(CH_3)_2NH_2^+$	0.36	−0.4	−0.4	2.5	−0.15
	$(CH_3)_3NH^+$	0.39	−0.3	−0.4	1.6	−0.21
	$(CH_3)_4N^+$	0.38	0.1	0.1	1.6	0.04
	$(C_2H_5)_4N^+$	0.45	0.6	0.6	0.7	0.83
	$(n\text{-}C_3H_7)_4N^+$	0.43	0.6	0.6	0.5	1.05
	$(n\text{-}C_4H_9)_4N^+$	0.28	−0.3	−0.3	0.3	−1.06

increasing or decreasing the $-(\bar{\bar{s}}_0-s_0)$ with counterions was similar to that of $-D$, because D^* monotonously decreases with increasing the hydrophobic alkyl groups of the counterions. The alternation of $(\bar{\bar{s}}_0-s_0)$ depends on the $\bar{\bar{s}}_0$, reflecting the state of water in the membrane, since s_0 is nearly constant regardless of the counterions.

For Aciplex® K-181 and K-182, the value of $\bar{\bar{s}}_0$ was always higher than s_0 in the ammonium and the alkylated ammonium halide solutions, and thermoosmosis occurred from the hot side to the cold side. For Neosepta® C66-5T, $\bar{\bar{s}}_0$ was lower than s_0 in $(CH_3)_4NCl$, $(C_2H_5)_4NBr$, and $(n\text{-}C_3H_7)_4NBr$ solutions. These counterions, since they have no exchangeable hydrogens, will act to order the structure of water in the membranes having a high water content. In fact, as shown in Table 2, the water content of Neosepta® C66-5T was much larger than those of Aciplex® K-181 and K-182. Therefore, thermoosmosis occurred from the cold side to the hot side, just like for anion-exchange membranes.

The enthalpy differences for the ammonium and the alkylated ammonium ion forms $\Delta h_0=-T(\bar{\bar{s}}_0-s_0)$ were from −2.55 to −0.07 kJ mol^{-1} for Aciplex® K-181, −1.66 to 0.07 kJ mol^{-1} for Aciplex® K-182, and −0.33 to 0.32 kJ mol^{-1} for Neosepta® C66-5T, when one mole of water was transported from the external solution phase into the membrane phase at $T=308.2$ K.

For perfluorosulfonic acid-type membranes[6] and hydrocarbonsulfonic acid-type membranes, the states of water in the membranes are sensitive to the species of the counterions. If the counterions are ammonium or alkylated ammonium ions, the hydrogen combining with the nitrogen of counterions can exchange with the hydrogen of the adjacent water. In these cases, the entropy of water in the membrane becomes high, that is, the state of water is unstable. And also, if the counterions have bulky hydrophobic alkyl groups, the attractive forces act between the counterions and the

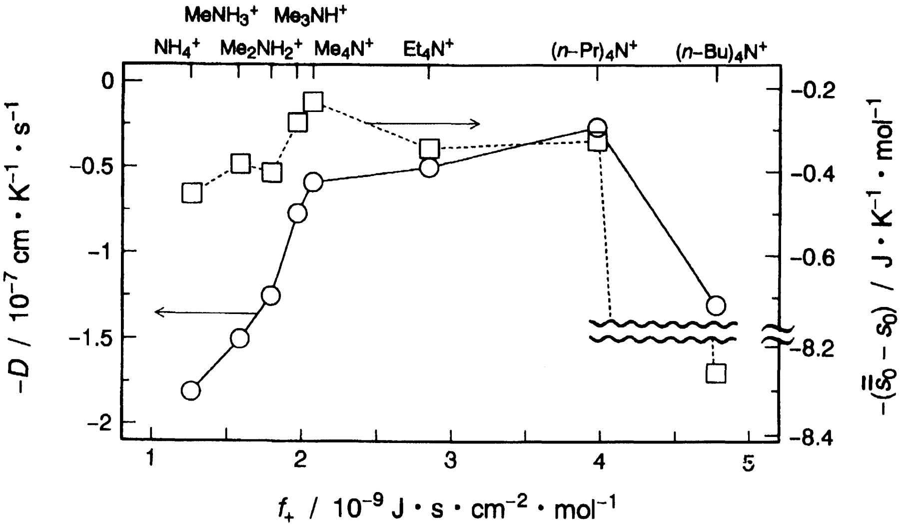

Fig. 8. The dependence of thermoosmotic coefficients, $-D$ (○), and the entropy difference of water, $-(\bar{\bar{s}}_0-s_0)$ (□), on the friction coefficient of the counterions, f_+, for Aciplex® K-181 with the ammonium and the alkylated ammonium ion forms.

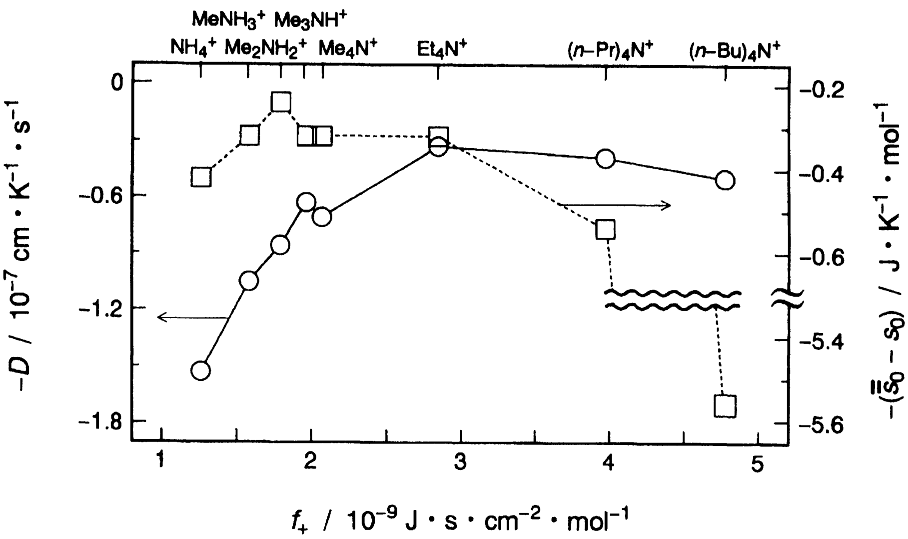

Fig. 9. The dependence of thermoosmotic coefficients, $-D$ (○), and the entropy difference of water, $-(\bar{\bar{s}}_0-s_0)$ (□), on the friction coefficient of the counterions, f_+, for Aciplex® K-182 with the ammonium and the alkylated ammonium ion forms.

membrane matrix and/or between the counterions. The membranes with these counterions act just as hydrophobic hydrocarbon membranes. In the hydrophobic polymer membranes having no fixed charges, the state of water is unstable.[17] Therefore, for these membranes, the transportation of water from the external solution phase into the membrane phase occurs under an endothermic condition and thermoosmosis occurs toward the cold solution side.

Conclusions

1) For hydrocarbonsulfonic acid-type membranes with the H^+ forms, the volume flux under a temperature difference and/or an osmotic pressure difference was very high because of the proton transfer between the counterions and the adjacent water molecules.

2) The thermoosmotic coefficient, D, and the entropy difference, $(\bar{\bar{s}}_0-s_0)$, increase with increasing the number of hydrogens combining with the nitrogen of the alkylated ammonium counterions and with increasing the hydrophobicity of the alkylated ammonium of counterions.

We wish to thank Asahi Chemical Industry Co., Ltd. and Tokuyama Soda Co, Ltd. for supplying the membranes Aciplex® and Neosepta®, respectively.

List of Symbols

The subscripts 0 and + refer to water molecules and cations, respectively.

$\bar{c}_0$ the concentration of water in the membrane phase

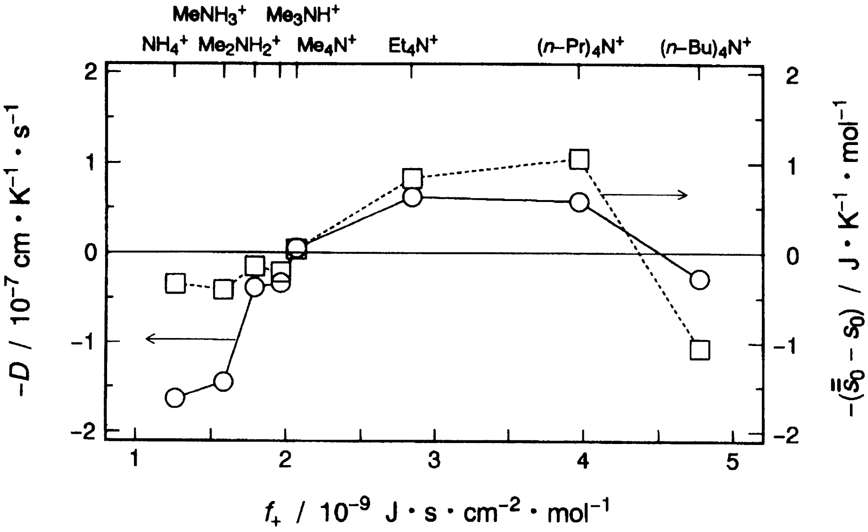

Fig. 10. The dependence of thermoosmotic coefficients, $-D$ (○), and the entropy difference of water, $-(\bar{\bar{s}}_0-s_0)$ (□), on the friction coefficient of the counterions, f_+, for Neosepta® C66-5T with the ammonium and the alkylated ammonium ion forms.

	(mol cm^{-3})
D	thermoosmotic coefficient (cm K^{-1} s^{-1})
D°	thermoosmotic coefficient: $D^\circ=D/f$ (cm K^{-1} s^{-1})
D^*	coefficient defined by Eq. 2 (cm mol J^{-1} s^{-1})
$D^{*\circ}$	coefficient: $D^{*\circ}=D^*/f$ (cm mol J^{-1} s^{-1})
d	the movement of the liquid meniscus (cm)
F	Faraday constant (96485 C mol^{-1})
f	tortuosity factor
f_+	friction coefficient of cations (J s cm^{-1} mol^{-1})
$f_{\mathrm{Li}}D^\circ$	thermoosmotic coefficient at the same water content as that with the Li$^+$ form (cm K^{-1} s^{-1})
g	osmotic coefficient
h_0	molar enthalpy of water (J mol^{-1})
J_v	volume flux (cm s^{-1})
L_p	hydraulic permeability (cm Pa^{-1} s^{-1})
l°_{v0}	phenomenological coefficient related to the mobility of water in the membrane (cm^5 J^{-1} s^{-1})
l°_{v+}	phenomenological coefficient related to the interaction between the cations and water (cm^5 J^{-1} s^{-1})
R	gas constant (8.314 J K^{-1} mol^{-1})
R_m	membrane resistance (Ω cm^2)
s_0	partial molar entropy of water in the external solution (J K^{-1} mol^{-1})
$\bar{\bar{s}}_0$	mean molar transported entropy of water in the membrane (J K^{-1} mol^{-1})
T	absolute temperature (K)
t	time (s)
v_0	partial molar volume of water (cm^3 mol^{-1})
w_0	water content (g of H_2O per g of dry membrane without counterions)
Δ	difference across the membrane
ΔT	effective temperature difference across the membrane (K)
ΔT_b	temperature difference of bulk solutions (K)
Δc_s	concentration difference of the external salt solutions (mol cm^{-3})
$\Delta\pi$	osmotic pressure difference of the external salt solutions (Pa)
δ	thickness of the membrane (cm)
ν	number of moles of ions formed from 1 mole of electrolyte
τ_0	reduced transport number of water (mol C^{-1})
ϕ°	volume fraction of the liquid phase in the membrane
ϕX	effective concentration of fixed charges (mol cm^{-3})

References

1) M. Tasaka, T. Urata, R. Kiyono, and Y. Aki, *J. Membr. Sci.*, **67**, 83 (1992).

2) T. Suzuki, R. Kiyono, and M. Tasaka, *J. Membr. Sci.*, **92**, 85 (1994).

3) M. Tasaka, T. Hirai, R. Kiyono, and Y. Aki, *J. Membr. Sci.*, **71**, 151 (1992).

4) M. Tasaka, T. Suzuki, R. Kiyono, and O. Sekiguchi, *Proc. Int. Symp. Membr. Membr. Processes*, Hangzhou (1994), in press.

5) J. W. Lorimer, "Non-Isothermal Transport Phenomena in Charged Membranes," in "Charged Gels and Membranes Part 2," ed by E. Sélégny, D. Reidel, Dordrecht (1976), p. 45.

6) T. Suzuki, Y. Takahashi, R. Kiyono, and M. Tasaka, *Colloid Polym. Sci.*, **272**, 971 (1994).

7) M. Tasaka and M. Nagasawa, *Biophys. Chem.*, **8**, 111 (1978).

8) J. S. Mackie and P. Meares, *Proc. R. Soc. London, Ser. A*, **232A**, 498 (1955).

9) T. Ueda, N. Kamo, N. Ishida, and Y. Kobatake, *J. Phys. Chem.*, **76**, 2447 (1972).

10) Y. Mizutani, *J. Membr. Sci.*, **49**, 121 (1990).

11) H. Uedaira and H. Uedaira, *Zh. Phiz. Khim.*, **42**, 3024 (1968).

12) H. Uedaira and A. Ohsaka, "Seitai-Kei no Mizu (Water in Biological Systems)," Kodan-Sha, Tokyo, Japan (1989), p. 54.

13) E. R. Nightingale, Jr., "On the Specificity of Electrolyte Solvation," in "Chemical Physics of Ionic Solutions," ed by B. E. Conway and R. G. Baradas, John Wiley & Sons, Inc., New York, London, and Sydney (1966), Chap. 7.

14) U. P. Strauss and N. L. Gershfeld, *J. Phys. Chem.*, **58**, 747 (1954).

15) S. Lindenbaum and G. E. Boyde, *J. Phys. Chem.*, **68**, 911 (1964).

16) R. A. Robinson and H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London (1959), p. 476.

17) M. Tasaka, T. Mizuta, and O. Sekiguchi, *J. Membr. Sci.*, **54**, 191 (1990).